

APPLICATION
FOR
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TITLE: METHOD OF FABRICATING ELECTRO-OPTIC
POLYMER WAVEGUIDE DEVICES INCORPORATING
ELECTRO-OPTICALLY ACTIVE POLYMER CLADS

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Method of Fabricating Electro-optic Polymer Waveguide Devices Incorporating Electro-optically Active Polymer Clads

Related Applications

5 This application is a continuation-in-part (and claims the benefit of priority under 35 USC 120) of U.S. application serial no. 10/299,155, filed November 19, 2002. The disclosure of the prior application is considered part of (and is incorporated by reference in) the disclosure of this application.

Background of the Invention

10 All patents, patent applications, and publications cited within this application are incorporated herein by reference to the same extent as if each individual patent, patent application or publication was specifically and individually incorporated by reference.

 The invention relates generally to the field of electro-optic polymer waveguide
15 devices. The art of electro-optic polymer waveguide devices and the use of organic second order nonlinear optical polymers in such devices is well documented. A typical electro-optic polymer waveguide, which is illustrated as a cross-sectional view in Figure 1, is comprised of: 1) an electro-optic polymer core (5); 2) a first polymer clad (10) overlying the electro-optic polymer core (5); 3) a second polymer clad (15) underlying
20 the electro-optic polymer core (5); 4) a top electrode (20) overlying the first polymer clad (10); 5) a bottom electrode (25) underlying the second polymer clad (15); and 6) a substrate (30).

 In a typical electro-optic polymer waveguide, the total thickness of the core, first clad, and second clad is around 6-10 μm . Typically, the refractive indices of the polymer
25 clads are chosen to confine a great majority of the optical field in the electro-optic polymer core and keep the optical field from contacting the metal electrodes. The resulting mode in the waveguide is elliptical to such an extent that unacceptably high insertion results when the waveguide is butt-coupled to an optical fiber. The insertion loss can be reduced by using tapers to adjust the size of the fiber mode to the size of the
30 waveguide mode. However, such tapers can be difficult to manufacture.

 Making the waveguide mode less elliptical can also reduce insertion loss. A less elliptical waveguide mode can be achieved by decreasing the difference in refractive

indices between the clads and electro-optic core. However, such an approach may lead to the optical field contacting one or both of the electrodes, which may cause increased optical loss or complete loss of mode confinement. Such a problem may be overcome by adding lower refractive index clads to act as barriers between the first and second clads
5 and metal electrodes.

U.S. Patent 5,861,976 describes a thermo-optic waveguide having four cladding layers in order to reduce insertion loss while confining the mode away from the silicon substrate and metal heater strip. The first and second “core matching” cladding layers have refractive indices that are 0.0055 lower than the core, while the third and fourth
10 cladding layers have refractive indices that are 0.0215 lower than the first and second cladding layers. The overall device thickness is around 20 μm . The insertion loss of the device is reportedly 2 dB/cm. Although the thermo-optic device showed good (i.e., low) insertion loss, such a device structure applied to electro-optic waveguides would lead to poor power performance since the electrodes are farther away from the electro-optic core
15 than in a typical electro-optic waveguide device; the problem would be compounded since a lesser percentage of light propagates in the core relative to typical electro-optic device structures.

Summary of the Invention

20 An electro-optic waveguide device is described that includes an electro-optic polymer core having a refractive index and an electro-optic first polymer clad in proximity to the electro-optic polymer core. By “in proximity to” it is meant that the core and clad are in contact with each other or separated by a thin (e.g., on the order of about 0.1 μm or so) adhesion promoter, surface promoter, or primer layer, as is known in the
25 art. The refractive index of the clad is lower than the refractive index of the core. The waveguide may further include, alone or in combination with each other: (a) a second polymer clad in proximity to the electro-optic core, the second polymer clad having a refractive index that is lower than the refractive index of the core; (b) a first polymer buffer clad in proximity to the electro-optic first polymer clad, the first polymer buffer
30 clad having a refractive index that is lower than the refractive index of the electro-optic first polymer clad; and (c) a second polymer buffer clad in proximity to the second

polymer clad, the second polymer buffer clad having a refractive index that is lower than the refractive index of the second polymer clad. As used herein, a “buffer clad” is the outermost layer from the core of the waveguide and has a refractive index sufficiently low to keep the optical mode from contacting electrodes that would cause optical loss (e.g., gold electrodes).

The electro-optic first polymer clad increases the power efficiency of the device since some of the propagating mode resides in the first polymer clad. Additionally, the structure also decreases optical insertion loss since the propagating mode is both less elliptical and does not contact the metal electrodes due to the buffer clads.

Another embodiment is a method of fabricating a polymer waveguide comprising (a) forming a first polymer film in proximity to a substrate, where the first polymer film comprises a nonlinear optical chromophore; (b) poling and crosslinking the first polymer film to provide a crosslinked first electro-optic polymer film; (c) forming a second polymer film comprising a nonlinear optical chromophore in proximity to the first electro-optic polymer film; and (d) poling the second polymer film to provide a second electro-optic polymer film. The refractive index of the second electro-optic polymer film may be lower than the refractive index of the first electro-optic polymer film or refractive index of the first electro-optic polymer film may be lower than the refractive index of the second electro-optic polymer film.

Other features and advantages will be apparent from the following description of the preferred embodiments, and from the claims.

Brief Description of the Drawings

Figure 1 illustrates a typical prior art electro-optic polymer waveguide device.

Figure 2 is a cross-sectional view of one embodiment of an electro-optic polymer waveguide device.

Figure 3 is a cross-sectional view of various electro-optic core configurations in the polymer stack.

Figure 4 is a cross-sectional view of another embodiment of an electro-optic polymer waveguide device.

Detailed Description

In one embodiment, an electro-optic waveguide device comprises an electro-optic polymer core and an electro-optic first polymer clad in proximity to the electro-optic polymer core, the electro-optic first polymer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core. The electro-optic first polymer clad increases the power efficiency of the device since some of the propagating mode resides in the first polymer clad. Both the electro-optic core polymer layer and the electro-optic clad polymer layer can be formed by methods known to those skilled in the art such as spin-coating, dip-coating, brushing, and printing.

In general, an electro-optic polymer comprises a second order nonlinear optical chromophore and a polymer matrix. In some embodiments, the chromophore can be covalently attached to the polymer backbone. The electro-optic core can be poled by any one of the techniques known to those skilled in the art including corona poling, electrode poling, or push-pull poling. The electro-optic core can be shaped by reactive ion etching, laser ablation, bleaching, positive tone photolithography, negative tone photolithography, or embossing. Referring to Figure 3, the electro-optic core can be shaped as a "rib" (Figure 3a), a "quasi-rib" (Figure 3b), a "quasi-trench" (Figure 3c), or a "buried-trench" (Figure 3d). Preferably, the electro-optic device is a Mach Zehnder modulator, a directional coupler, or a micro-ring resonator.

In a preferred embodiment, the electro-optic waveguide device comprises, referring to Figure 2: 1) an electro-optic polymer core (35); 2) an electro-optic first polymer clad (40) in proximity to the electro-optic polymer core, the electro-optic first polymer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core; 3) a second polymer clad (45) in proximity to the electro-optic polymer core, the second polymer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core; 4) a first polymer buffer clad (50) in proximity to the electro-optic first polymer clad, the first polymer buffer clad having a refractive index that is lower than the refractive index of the electro-optic first polymer clad; and 5) a second polymer buffer clad (55) in proximity to the second polymer clad, the second polymer buffer clad having a refractive index that is lower than the refractive index of the second polymer clad. The electro-optic polymer core, electro-optic first

polymer clad, second polymer clad, first polymer buffer clad, and second polymer buffer clad can each be formed independently by methods known to those skilled in the art such as spin-coating, dip-coating, brushing, and printing. In another embodiment, the second polymer clad is an electro-optic polymer or, preferably, a crosslinked electro-optic polymer.

In another embodiment, the electro-optic waveguide device comprises, referring to Figure 4: 1) an electro-optic polymer core (35); 2) an electro-optic first polymer clad (40) in proximity to the electro-optic polymer core, the electro-optic first polymer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core; 3) a first polymer buffer clad (50) in proximity to the electro-optic first polymer clad, the first polymer buffer clad having a refractive index that is lower than the refractive index of the electro-optic first polymer clad; and 4) a second polymer buffer clad (55) in proximity to the electro-optic polymer core, the second polymer buffer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core. The electro-optic polymer core, electro-optic polymer first clad, first polymer buffer clad, and second polymer buffer clad can each be formed independently by methods known to those skilled in the art such as spin-coating, dip-coating, brushing, and printing.

The refractive index and thickness of each polymer layer is chosen so that the resulting waveguide has single mode behavior. The refractive index of each layer, thickness of each clad, and the dimensions of the core that would give single mode behavior in the resulting waveguide can be calculated using techniques and computer programs known to those skilled in the art (such as the BeamProp Version 5.0 software from Rsoft). Preferable ranges for the thickness and the refractive index of the various layers are summarized in Table 1. Preferably, referring to Figure 2, the electro-optic core (35) is shaped as a rib and has a thickness of about 2.4 – about 3.8 μm and a refractive index of about 1.54 – about 1.62, the electro-optic first polymer clad (40) has a thickness between the electro-optic core surface (60) and the electro-optic first polymer clad surface (65) of about 1.0 – about 3.0 μm and a refractive index of about 1.53 – about 1.61, the second polymer clad (45) has a thickness of 0 – about 3.0 μm and a refractive index of about 1.53 – about 1.61, the first polymer buffer clad (50) has a thickness of

about 2.2 – about 3.2 μm and a refractive index of about 1.445 – about 1.505, and the second polymer buffer clad has a thickness of about 2.2 – about 3.2 μm and a refractive index of about 1.445 – about 1.505. The preferable ranges for refractive index, layer thickness, and core dimensions for the various layers are given below in Table 1.

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Table 1

Layer	Thickness (μm)	Width (μm)	Refractive Index
First Polymer Buffer Clad	2.2 – 3.2	-	1.445 – 1.505
First Polymer Clad	1.0 – 3.0	-	1.53 – 1.61
Core	2.4 – 3.8	2.8 – 4.2	1.54 – 1.62
Second Polymer Clad	0 – 3.0	-	1.53 – 1.61
Second Polymer Buffer Clad	2.2 – 3.2	-	1.445 – 1.505

In another embodiment, the electro-optic core is crosslinked, the electro-optic first polymer clad is crosslinked, the second polymer clad is an organically modified sol-gel (ORMOSIL), the first polymer buffer clad is a radiation-cured acrylate, and the second polymer buffer clad is an organically modified sol-gel. Crosslinkable electro-optic polymers, sol-gels, ORMOSILs, and radiation cured acrylates are known to those skilled in the art, for example see US Pat. No. 6,419,989; 6,335,149; 6,323,361; 6,306,563; 6,303,730; 6,294,573; 6,126,867; 6,002,828; 5,811,507; 5,783,319; 5,776,374; 5,635,576; 5,714,304; 5,480,687; 5,433,895; 5,223,356; and 5,120,339; *Chem. Mater.* **2000**, *12*, 1187; *J. Am Chem. Soc.* **2001**, *123*, 986; *Macromolecules* **1992**, *25*, 4032; and *Chem. Mater.* **1998**, *10*, 146. Preferably, the second polymer clad comprises a titanium doped organically modified sol gel.

The optical waveguide devices described herein comprising an electro-optic polymer core and an electro-optic first polymer clad having a refractive index that is lower than the refractive index of the electro-optic polymer core can be used in optical communications systems. The optical communications systems employing such modulators will be improved due to the increased power efficiency of the waveguide devices having an electro-optic polymer clad and an electro-optic polymer core. Thus,

other embodiments of the invention include communications systems such as beam steering systems, phased array radars, optical routers, optical transponders, and optical satellites.

Another embodiment is a method of fabricating a polymer waveguide comprising

5 (a) forming a first polymer film in proximity to a substrate, where the first polymer film comprises a nonlinear optical chromophore; (b) poling and crosslinking the first polymer film to provide a crosslinked first electro-optic polymer film; (c) forming a second polymer film comprising a nonlinear optical chromophore in proximity to the first electro-optic polymer film; and (d) poling the second polymer film to provide a second

10 electro-optic polymer film. Preferably, the substrate may comprise a polymer, an organically modified sol-gel, or an electro-optic polymer. Preferably, the second electro-optic polymer film is crosslinked. The refractive index of the second electro-optic polymer film is preferably lower than the refractive index of the first electro-optic polymer film. When the refractive index of the second electro-optic polymer film is

15 lower than the refractive index of the first electro-optic polymer film, preferably the first electro-optic film is dry etched to form a rib or quasi rib before forming the second polymer film comprising a nonlinear optical chromophore in proximity to the first electro-optic polymer film. The dry etching step can comprise using a metal hardmask, and the metal hardmask preferably comprises titanium or platinum. In many

20 embodiments, the rib or quasi rib is a Mach-Zehnder modulator, directional coupler, or micro-ring resonator. When the refractive index of the second electro-optic polymer film is lower than the refractive index of the first electro-optic polymer film, the first electro-optic polymer film may be formed as a rib, quasi rib, quasi-trench, or trench by methods comprising laser ablation, bleaching, positive tone photolithography, negative tone

25 photolithography, or embossing. In another embodiment, the substrate comprises a crosslinked electro-optic polymer. The method of forming a polymer waveguide may further comprise (e) forming a polymer buffer clad in proximity to the second electro-optic polymer film. When the method of forming a polymer waveguide further comprises forming a polymer buffer clad in proximity to the second electro-optic

30 polymer film, preferably the first electro-optic polymer film has a thickness of about 2.4 to about 3.8 μm and a refractive index of about 1.54 to about 1.62; the second electro-

optic first polymer film has a thickness of about 1.0 to about 3.0 μm and a refractive index of about 1.53 to about 1.61; and the polymer buffer clad has a thickness of about 2.2 to about 2.8 μm and a refractive index of about 1.445 to about 1.505. Preferably, the polymer buffer clad is crosslinked. The first electro-optic polymer film may also form a trench or quasi-trench. When the first electro-optic polymer film forms a trench or quasi-trench, the substrate preferably comprises a crosslinked electro-optic polymer. Preferably, the crosslinking of the first polymer film occurs above about 160 °C. When the first polymer film is crosslinked, preferably the film may be crosslinked during poling or crosslinked before poling. The first polymer film comprising a nonlinear optical chromophore or second polymer film comprising a nonlinear optical chromophore may be formed by methods comprising spin coating, dip coating, or brushing.

In another embodiment, the refractive index of the first electro-optic polymer is lower than the refractive index of the second electro-optic polymer. When the refractive index of the first electro-optic polymer is lower than the refractive index of the second electro-optic polymer, the method may preferably further comprise (e) dry etching the second electro-optic film to form a rib or quasi rib and (f) forming a polymer buffer clad in proximity to the second electro-optic polymer film. The polymer buffer clad is preferably crosslinked. In another embodiment when the refractive index of the first electro-optic polymer is lower than the refractive index of the second electro-optic polymer, the second electro-optic polymer film may form a quasi-trench or trench. When the second electro-optic polymer film forms a quasi-trench or trench, preferably the method further comprises (e) forming a first polymer buffer clad in proximity to the second electro-optic polymer film. Preferably, the polymer buffer clad is crosslinked. When the refractive index of the first electro-optic polymer is lower than the refractive index of the second electro-optic polymer, the second electro-optic polymer film may be formed as a rib quasi rib, quasi-trench, or trench by methods comprising laser ablation, bleaching, positive tone photolithography, negative tone photolithography, or embossing

Examples

The following example(s) is illustrative and does not limit the Claims.

The preparation of materials used in the following example is given below:

The electro-optic chromophore used in the electro-optic core and electro-optic clad was prepared by esterifying a chromophore containing free alcohol groups with the required equivalents of 4-(trifluorovinyloxy)-benzoyl chloride (the benzoyl chloride is
5 described in U.S. Pat. 5,198,513) and a hindered amine base or pyridine.

The polymer used as a matrix for the electro-optic chromophore was prepared by reacting 1-lithio-4-trifluovinyloxybenzene with pentafluorostyrene at -78°C for 1 h followed by warming to room temperature. The resulting 2,3,5,6-fluoro-4'-trifluorovinyloxy-4-vinyl biphenyl was purified by column chromatography and
10 polymerized with AIBN initiation in THF under N_2 atmosphere. The polymer was purified by precipitation from THF/hexanes.

The titanium doped organically modified sol gel used as the second polymer clad was prepared by: 1) dripping 127.2 g of titanium butoxide (from Aldrich, double distilled) into a solution of 592 g of anhydrous ethanol and 24.0 g of concentrated DCI
15 (~ 37 wt%); 2) dripping 94.3 g of D_2O ; 3) dripping 99.2 g of glycidoxypopyltrimethoxysilane; 4) heating at $\sim 80^{\circ}\text{C}$ for 12 hours; 5) dripping 372.0 g of phenyltriethoxysilane (from Aldrich, distilled) while at $\sim 80^{\circ}\text{C}$ for 4 hours; and 6) adding distilled 473 g of cyclohexanone into the solution and stir to homogeneity. The volatiles from the reaction were removed by rotary evaporation. Finally, 1.60 g of
20 poly[dimethylsiloxane - co- methyl(3-hydroxypropyl)siloxane] – graft - poly(ethylene/-propylene glycol) (from Aldrich, used as received) was added into the above solution and stirred to obtain a homogeneous solution.

The polymer used as the first polymer buffer clad was prepared by: 1) stirring 20.0 g of pentaerythritol tetraacrylate (Aldrich, used as received) and 20.0 g tri(ethylene
25 glycol) dimethacrylate (Aldrich, used as received); 2) adding 1.2 g of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone and stirring until dissolution; and 3) refrigerating the resulting solution.

The polymer used as the second polymer buffer clad was prepared by: 1) adding 156.0 gram tetraethyl orthosilicate (from Aldrich, double distilled), 531.0 g
30 glycidoxypopyl-trimethoxysilane (from Aldrich, double distilled), 321.0 g

cyclohexanone (from Aldrich, distilled) to a flask; 2) dripping a solution of 187.5 g D₂O and 7.50 g 2M DCl; and 3) heating at 80-100°C for 5 hours.

An adhesion promoter for the second polymer buffer clad and gold was prepared by: 1) heating 100.0 g of isopropyl alcohol (from Aldrich), 2.0 g of H₂O, 5.0 g of
 5 mercapto-propyltriethoxysilane (from Sigma, distilled) and 5.0 g of mercaptopropylmethyl-dimethoxysilane, and two drops of 37% HCl at reflux for 2 hours; 2) allowing the solution cool down to room temperature; 3) adding 504 g of isopropyl alcohol to the above solution and stirring.

10 The device in this example was fabricated using a goldcovered SiO₂ 6-inch wafer as a substrate.

The adhesion promoter for the second polymer buffer clad and gold was applied to the gold surface by spin depositing a 1% solution at 500 rpm for 2 seconds and 4500 rpm for 30 seconds.

15 The second polymer buffer clad was spin deposited as a 36.1% (by weight) solution in cyclopentanone at 300 rpm for 12 seconds and 1050 rpm for 20 seconds. The wafer layer was cured by heating under 50 Torr of vacuum at 100 °C for 60 min (heating rate of 0.5 °C/min), 150 °C for 60 min (heating rate of 3 °C/min), and 200 °C for 30 min (heating rate of 5 °C/min), and cooling the wafer to ambient temperature at a cooling rate of 0.5 °C/min. The thickness of the layer is 2.9 μm and the refractive index is 1.475.

20 The second polymer clad was spin deposited on the second polymer buffer clad as a 38% (by weight) solution in cyclohexanone at 500 rpm for 5 seconds and 2900 rpm for 30 seconds. The wafer layer was cured by heating under 50 Torr of vacuum at 100 °C for 60 min (heating rate of 0.5 °C/min), 150 °C for 60 min (heating rate of 3 °C/min), and 190 °C for 90 min (heating rate of 5 °C/min), and cooling the wafer to ambient
 25 temperature at a cooling rate of 0.5 °C/min. The thickness of the layer was 1.9 μm and the refractive index was 1.545.

An adhesion promoter layer was applied to the second polymer clad by spin depositing a 1% (by weight) solution of poly(*N*-(2-aminoethyl)-3-aminopropylmethyl-dimethoxysilane) in isopropyl alcohol at 500 rpm for 5 sec and 3000 rpm for 30 sec. The
 30 wafer was then heated on a hot plate at 100 °C for 5 min.

The polymer used for the electro-optic core was spin deposited on the second polymer clad as a 30% (by total solids weight) solution of the electro-optic chromophore in the polymer matrix (the chromophore concentration with respect to the crosslinkable polymer was 25% by weight) in cyclopentanone at 300 rpm for 2 sec then 500 rpm for 5 sec, then 1000 rpm for 20 sec. The film was precured by heating at 80 °C on a hot plate for 10 min, heating at 70 °C at 1 mTorr for 480 min. The film was Corona poled and crosslinked by applying a voltage of 4.5 kV to the wafer while heating to 180 °C over 10 min, holding at 4.5 kV at 180 °C for 10 min, increasing the Corona voltage to 7.5 kV and holding at 180 °C for 10 min, and cooling to ambient temperature over 25 min. Heating at 180 °C was necessary to affect the desired amount of crosslinking. The thickness of the layer was 3.0 μm and the refractive index was 1.565.

The electro-optic polymer core was formed as a rib using a hardmask and dry etching as described in commonly assigned, co-pending US Application Ser. No. 10/264,461. The electro-optic polymer core was formed as a Mach-Zehnder Modulator.

The polymer used for the electro-optic first polymer clad was spin deposited on the electro-optic core and the second polymer clad as a 23% (by total solids weight) solution of the electro-optic chromophore in the polymer matrix (the chromophore concentration with respect to the crosslinkable polymer was 21% by weight) in cyclopentanone at 300 rpm for 2 sec then 500 rpm for 5 sec, then 1400 rpm for 20 sec. The film was precured by heating at 50 °C on a hot plate for 10 min followed by heating at 25 Torr for 8 h at 50 °C. The film was corona poled and crosslinked by applying a voltage of 7.5 kV to the wafer while heating at 180 °C for 20 min. The thickness of the layer was 1.2 μm and the refractive index was 1.55.

The first polymer buffer clad was spin deposited on the electro-optic first polymer clad as a liquid at 500 rpm for 5 seconds and 1800 rpm for 40 seconds. The wafer was then exposed to UV radiation until the film was hardened. The thickness of the layer was 3.1 μm and the refractive index was 1.495.

The surface of the first polymer buffer clad was treated with oxygen/neon plasma for 7 min in order to promote adhesion of a gold layer. The gold layer was deposited and the gold electrode was defined over one arm of the Mach-Zehnder modulator by

photolithography and wet etching. The wafer was diced into individual Mach-Zehnder electro-optic devices.

Other embodiments are within the following claims.